

# Temperature Renormalization of Optical Spectra of Monolayer MoS<sub>2</sub>

Ryan Soklaski,<sup>†</sup> Yufeng Liang,<sup>†</sup> Changjian Zhang,<sup>‡</sup> Haining Wang,<sup>‡</sup> Farhan  
Rana,<sup>‡</sup> and Li Yang<sup>\*,†</sup>

*Department of Physics, Washington University in St. Louis, St. Louis, MO 63136, USA, and  
School of Electrical and Computer Engineering, Cornell University, Ithaca, New York 14853,  
USA*

E-mail: lyang@physics.wustl.edu

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## Abstract

Newly measured optical absorption and photoluminescence spectra reveal substantial frequency shifts of both exciton and trion peaks as monolayer MoS<sub>2</sub> is cooled from 363 K to 4 K. First-principles simulations using the GW-Bethe-Salpeter Equation approach satisfactorily reproduce these frequency shifts by incorporating many-electron interactions and the thermal expansion of the in-plane lattice constant. Studying these temperature effects in monolayer MoS<sub>2</sub> is crucial for rectifying the results of room-temperature experiments with the previous predictions of zero-temperature-limit simulations. Moreover, we estimate that the thermal expansion coefficient of monolayer MoS<sub>2</sub> is around 25 % less than that of bulk counterpart by tracking the frequency shifts of the exciton or trion peaks in optical spectra. This may serve

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\*To whom correspondence should be addressed

<sup>†</sup>Department of Physics, Washington University in St. Louis, St. Louis, MO 63136, USA

<sup>‡</sup>School of Electrical and Computer Engineering, Cornell University, Ithaca, New York 14853, USA

as a convenient way to estimate thermal expansion coefficients of general two-dimensional chalcogenides.

Recently, much focus from the physics, chemistry, and material science communities has been directed on the unique electronic, magnetic, and optical properties of two-dimensional (2D) molybdenum and tungsten chalcogenides, such as MoS<sub>2</sub>.<sup>1-6</sup> Essential properties of monolayer MoS<sub>2</sub> and similar materials have been heavily scrutinized by experimental and theoretical studies. In particular, enhanced many-electron effects, including excitons and trions, have been identified by first-principles simulations, and their results have been widely applied to compare and explain experimental measurements.<sup>7-11</sup> However, the comparison of different simulations with experimental data has proven to be controversial.

Despite the rigor and intensity with which monolayer MoS<sub>2</sub> has been studied, a subtle yet important oversight persists: current experimental measurements of the optical absorption spectrum of the system are made at the room temperature,<sup>1,2</sup> while available first-principle calculations simulate monolayer MoS<sub>2</sub> at the 0-K limit. The marked resemblance between these experimentally and theoretically derived spectra<sup>8-11</sup> has made their comparison, without regard to the temperature discrepancy, pervasive, although temperature effects have been known to impact band gaps and optical spectra of bulk semiconductors. Diamond and silicon crystals are ready examples, in which many-electron effects and electron-phonon (*e-ph*) interactions induce band-gap renormalization according to temperature variations.<sup>12,13</sup> In this sense, considering temperature effects may be crucial for rectifying recent discrepancies between theory and experiments.

Beyond affecting electronic structures themselves, temperature-related many-electron excitations provide precious information for detecting thermal properties of atomistic structures. Previous studies show that the variation of the lattice constant of monolayer MoS<sub>2</sub> will induce substantial changes in its absorption spectra.<sup>14</sup> Therefore, by tracking optical excitations versus temperature, we may be able to infer the lattice variation with changing temperature, and obtain thermal expansion coefficient (TEC), which is a fundamental character of 2D structures but challenging to be measured directly. For instance, the TEC of graphene and their unique thermal behaviors have

been intensively studied.<sup>15–17</sup>

In this Letter, experimentally measured optical absorption spectra and photoluminescence (PL) measurements taken from 4 K to 363 K are presented alongside complementary first-principle results about monolayer MoS<sub>2</sub>. The measurements reveal that temperature changes significantly impact optical excitations, including the positions of exciton and trion peaks, and induce frequency shifts of up to 50 meV in the absorption peak positions. Simulations rooted in the GW-Bethe Salpeter equation (BSE) not only provide an exceptional agreement with the absolute peak positions measured from experiments at the low-temperature limit but also indicate that the frequency shift can largely be attributed to the thermal expansion of the in-plane lattice constant. Accordingly, we estimate the TEC of monolayer MoS<sub>2</sub> from the shift of optical peaks and conclude that it is around 25% smaller than that of bulk MoS<sub>2</sub>. This provides a convenient way of estimating the TEC of 2D semiconductors.

Absorption measurements are performed on monolayer MoS<sub>2</sub> at different temperatures under a microscope with 100X objective in transmission configuration. The samples are prepared on quartz substrates by mechanical exfoliation, and the typical size of an exfoliated sample is  $\sim 200\mu m^2$ . Monolayer MoS<sub>2</sub> samples are identified under optical microscope and then confirmed by Raman spectroscopy.<sup>18</sup> The samples are annealed in vacuum at 363 K for 8 hours. The samples are then placed in a helium flow cryostat and measurements are taken at temperatures between 5 K and 363 K. A broadband halogen light source is used to illuminate the samples. The transmitted light is collected using a confocal microscope setup and is dispersed by a monochromator with a resolution of  $\sim 0.2$  nm. Absorption spectra are obtained by subtracting the relative transmission spectra from unity. Temperature-dependent PL of monolayer MoS<sub>2</sub> is collected and analyzed using the same setup. The laser intensity is kept at values less than  $\sim 200\mu W/\mu m^2$  to prevent damage to the samples.

The measured optical absorption spectrum of monolayer MoS<sub>2</sub> at 4 K is presented in Fig. 1 (a). The featured prominent peak and lower-energy peak are widely attributed to exciton and trion states, respectively.<sup>7</sup> It is important to note that these peak positions, at 4 K, reside systematically

at higher energies than do the peaks found in experimental data that is collected at room temperature.<sup>1,2</sup> Additional measurements of the optical absorption spectra taken at increasing temperatures up to 363 K provide detailed energy-temperature trajectories for the exciton and trion absorption peaks, as shown in Fig. 1 (c). The absorption spectrum at 300K generally agrees with previous experimental results,<sup>1,2</sup> and ultimately reveals that both the exciton and trion peak positions incur red shifts of roughly 50 meV relative to their 4 K values. Corresponding PL spectra measurements indicate similar frequency shifts, as shown in Fig. 1 (d).

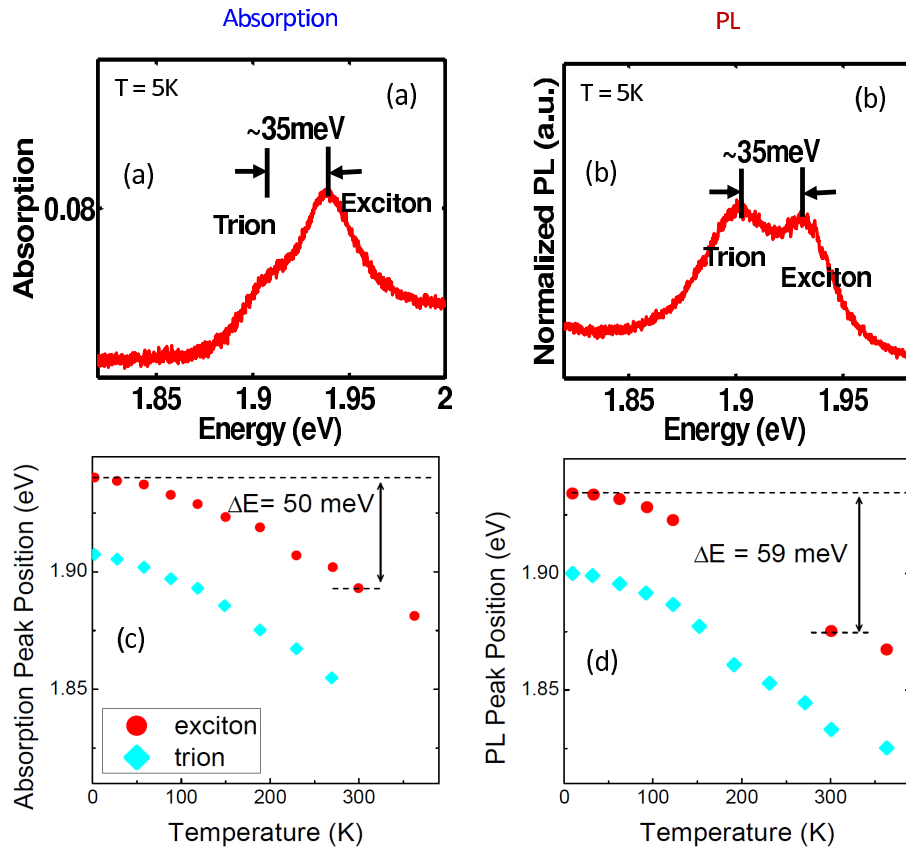


Figure 1: (Color online) (a) The optical absorption spectrum of monolayer MoS<sub>2</sub> at 4 K. (b) The PL spectrum of monolayer MoS<sub>2</sub> at 4 K. (c) The optical absorption peak positions of excitons and trions vs temperature. (d) the PL peak positions of excitons and trions vs temperature.

In order to understand these frequency shifts, we focus on the impacts of lattice expansion for the following reasons: 1) Previous studies show that the variation of the lattice constant of monolayer MoS<sub>2</sub> will induce substantial changes in its absorption spectra.<sup>14</sup> 2) The exciton and

trion states of monolayer MoS<sub>2</sub> are fundamentally tied to its band gap. Accordingly, the energy-temperature trajectories plotted in Figs. 1 (c) and (d) show that these states display a similar temperature dependence and thus their frequency shifts likely share the same physical origin.

We thus present results from a first-principles simulation of fully relaxed monolayer MoS<sub>2</sub>, for which the in-plane lattice constant is varied to mimic thermal expansion effects. We also break all symmetries for more realistic simulations. The quasiparticle band structure and optical absorption spectrum is obtained for each structure for the sake of comparison with experimental results. The simulation uses density functional theory (DFT) and the single-shot G<sub>0</sub>W<sub>0</sub> approach,<sup>19</sup> which closely follows the approach taken in Ref.<sup>20</sup> A fine k-grid (60 x 60 x 1) in the first Brillouin zone (BZ) is interpolated from a coarse grid (24 x 24 x 1) when finding converged excitonic states. The optical absorption spectrum is then calculated by solving the BSE, incorporating four valence bands, four conduction bands, and using incident light polarized parallel to the monolayer sheet. Spurious interactions between neighboring layers are avoided by imposing a slab Coulomb truncation. Spin-orbital coupling is not considered in the simulations.

First, we focus on the zero-temperature limit structure, which is fully relaxed according to both forces and stresses. The in-plane lattice constant is 3.18 Å. The quasiparticle-corrected band structure of monolayer MoS<sub>2</sub> at 0 K is depicted in Fig. 2 (a). The calculated structure contains a direct band gap of size 2.63 eV. This gap is widened from its DFT value (1.69 eV) significantly by many-electron interactions because of depressed screening. The optical absorption spectra of monolayer MoS<sub>2</sub> at 0 K, with and without *e-h* interactions, are summarized in Fig. 2 (b). This low-dimensional semiconductor's spectrum is dramatically affected by *e-h* interactions, as is typical for such systems.<sup>21–23</sup> Including *e-h* interactions lowers the optical absorption edge from 2.63 eV to 2.01 eV, indicating a large *e-h* binding energy of 0.62 eV. The location of the first prominent peak is close to our low-temperature measurement (1.94 eV) shown in Fig. 1. It is also close to recent calculations;<sup>8–11</sup> the slight differences may be due to our denser coarse k-point grid, which does not change the quasiparticle band gap significantly but more affects the excitonic effects. Due to the similar reason, we observe one prominent absorption peak (marked as A1 in Fig. 2 (b)) around

the absorption edge, indicating that the experimentally observed double-peak feature<sup>2</sup> results from spin-orbital coupling, which is not included in this simulation.

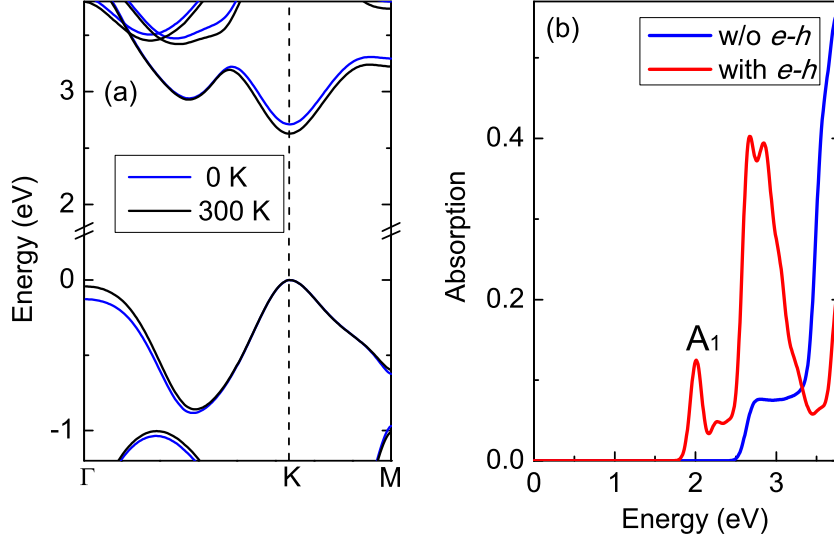


Figure 2: (Color online) (a) The quasiparticle band structure of monolayer MoS<sub>2</sub>. The blue curves are about zero temperature while the dark curves include the lattice expansion at 300 K. (b) The optical absorption spectra of monolayer MoS<sub>2</sub> at zero temperature with and without  $e$ - $h$  interactions included, respectively. A 0.06-eV Gaussian smearing is applied to obtain the smoothed spectra.

Next, we consider effects due to lattice thermal expansion. Presently, there is no available experimental data detailing the expansion of monolayer MoS<sub>2</sub> as temperature is varied. It is therefore natural to reference measured TEC values in multilayer MoS<sub>2</sub><sup>24</sup> for our calculations. The presence of only weak van der Waals (vdW) interactions between the bulk layers suggests that the TEC of monolayer MoS<sub>2</sub> would not vary drastically from that of multilayer MoS<sub>2</sub>. Fig. 3 shows that the experimentally measured lattice constant grows from roughly 3.13 to 3.15 when temperature is increased from 0 K to 300 K, around a 0.6% expansion. Using this TEC, the theoretical lattice constant for monolayer MoS<sub>2</sub> is increased from 3.18 to 3.20 to mimic the increase in temperature. The resulting quasiparticle band structure is presented in Fig. 2 (a). One can immediately note the reduced band gap, which has shrunk from 2.63 eV to 2.55 eV as the lattice expanded. This is qualitatively consistent with the red shift seen in the experimental optical absorption spectra (Figs. 1 (a) and (c)). The calculated optical absorption spectra, with  $e$ - $h$  interactions included,

are depicted in Fig. 4 (a) for the effective 4 K and 300 K lattice constants. The lattice expansion induces a 67-meV red shift of the exciton peak from 2.01 eV to 1.95 eV. It is promising to see that *the effects of expanding the lattice in the calculations satisfactorily agree with the experimentally observed temperature effects, which are characterized by a 50 meV red shift.*

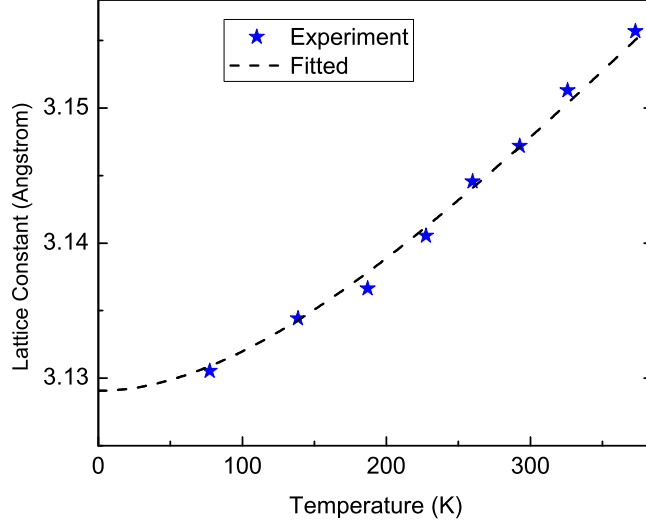


Figure 3: (Color online) The in-plane lattice constant of bulk MoS<sub>2</sub> variation according to the temperature. The blue stars are experimental data<sup>24</sup> and the dashed line is the fitted curve, respectively.

The presented measured and calculated results for monolayer MoS<sub>2</sub> allow for a more realistic comparison of the experimentally and theoretically derived optical absorption spectra. In the low-temperature limit, the measured and theoretical values for the exciton peak position are 1.94 eV and 2.01 eV, respectively. At room temperature, these respective values are red shifted to 1.89 eV and 1.94 eV. Moreover, if the spin-orbital splitting (around 140 meV<sup>10,11</sup>) is included approximately, the optical absorption edge will be lowered by about 70 meVs, locating the absorption peak at 1.94 eV. This is exceptionally consistent with the low-temperature measurement in Fig. 1 (a). Although this perfect consistence may not be conclusive because slight changes of simulation setups can easily vary the result for a few tens meVs, the present theoretical treatment of monolayer MoS<sub>2</sub>, with the thermal expansion included, shall be in even better agreement with experiment, which is outstanding for a parameter-free calculation.

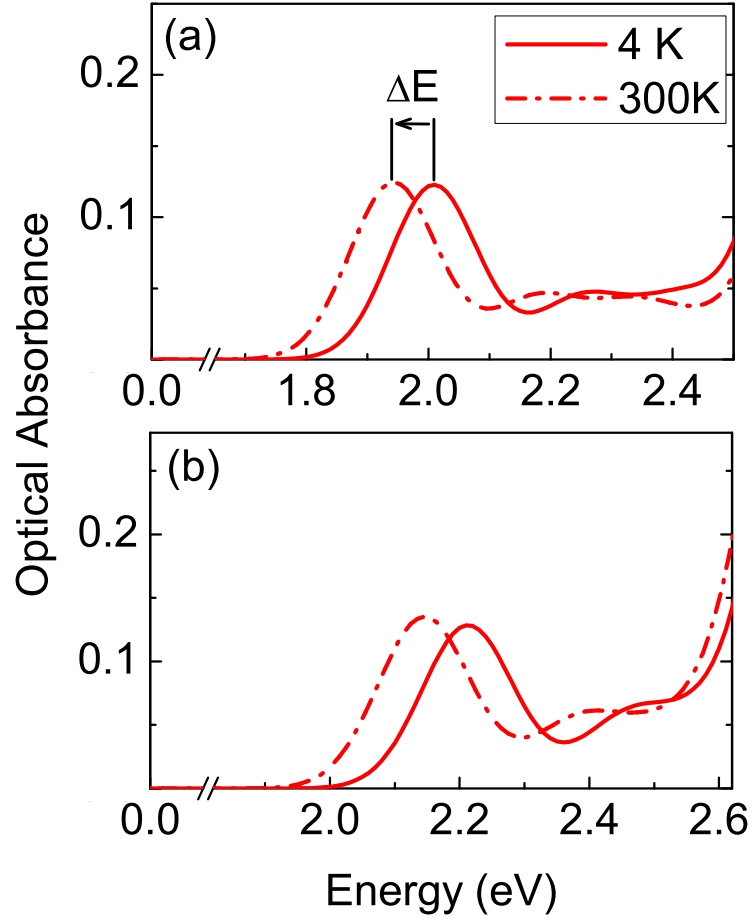


Figure 4: (Color online) (a) The optical absorption spectra of monolayer MoS<sub>2</sub> under different temperature when considering the lattice thermal expansion effect. The zero-temperature lattice constant is the theoretically optimized structure under DFT/PBE. (b) The similar plots are in (a), but the zero-temperature lattice constant is the experimental one read from Fig. 2. Excitonic effects are included in all plots. A 60-meV Gaussian broadening is applied.



Additional calculations are performed using the lattice constants for bulk MoS<sub>2</sub>, as listed in Fig. 3,<sup>24</sup> because it is known that DFT-optimized lattice constant may be different from experimental measurements within 1%. In the low-temperature limit, an extrapolated lattice constant approximate to 3.13 Å is used. At room temperature, we use the bulk value 3.15 Å. The resulting optical absorption spectra, with *e-h* interactions included, is presented in Fig. 4 (b). The exciton peak positions at 4 K and 300 K are 2.20 eV and 2.13 eV, respectively, corresponding to a 65 meV red shift with increasing temperature. Importantly, the frequency shift of the exciton peak is thus nearly independent of the exact lattice constants used. In this sense, tracking the frequency shift of absorption peaks across temperatures serves as a convenient method of estimating the TEC of monolayer MoS<sub>2</sub>, and perhaps in other materials as well, since it is extremely challenging to directly measure the lattice constant of monolayer materials at low temperature.

It is important to consider other factors that may have affected the band gap and optical spectrum of MoS<sub>2</sub> in our experiments. Higher-order *e-ph* interactions are capable of renormalizing band gaps in carbon semiconductors, however MoS<sub>2</sub> contains relatively heavy constituents, thus it is expected that the adiabatic approximation is valid. Additionally, band-filling effects<sup>25,26</sup> are not expected to be significant given the 2.6 eV-wide direct gap seen in Fig. 2 (a), which diminishes thermal generation. Finally, our samples are on a SiO<sub>2</sub> substrate, which may affect many-electron effects by providing additional screening. According to previous works,<sup>30</sup> the variation of the screening will affect both *e-e* and *e-h* interactions, but in opposite directions. Therefore, the quasiparticle band gap may vary but the final optical spectra and their shift would not change significantly.

From the other point of view, the small difference of the shift of optical peaks between experiments and simulations may reflect the different TECs of monolayer and multilayer MoS<sub>2</sub>. Under the first-order approximation, the optical gap is linearly proportional to the lattice constant. Therefore, based on our simulation result, the TEC of monolayer MoS<sub>2</sub> is around 75% of that of bulk counterpart. This trend is similar to the TECs of graphene and graphite.<sup>15–17</sup>

In conclusion, comprehensive experimental measurements and theoretical simulations have

been performed to study the temperature effects on the electronic structure and optical excitations of monolayer MoS<sub>2</sub>. Optical absorption and PL measurements reveal that exciton and trion absorption peaks incur redshifts as temperature is increased. First-principles calculations reveal that these red shifts are mainly due to the thermal expansion of the in-plane lattice constant. These results provide a needed bridge between incongruent experiment and simulation conditions that have generally been overlooked until present. Additionally, it is demonstrated that tracking the shift of absorption peak positions with temperature serves as a convenient way of estimating the TEC of 2D MoS<sub>2</sub>.

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